

Improvement of Fluorinated Products Consumption in an Electrolysis Series for Primary Aluminum

Theodore Tchotang¹, Paul Vianey Nguenpy², Lucien Meva'a³, Bienvenu Kenmeugne⁴

^{1, 2, 3, 4}University of Yaoundé I, National Advanced School of Engineering,
Department of Industrial and Mechanical Engineering, CETIC, Yaoundé 3, Rue de Melen 3.382, Cameroon

Abstract: The problem solved in this paper concerns the improvement of the consumption of fluorinated products in an electrolysis series for the production of primary aluminum. It will be a question of reducing the specific consumption of aluminum fluoride (AlF₃) and of stabilizing the average excess rate to a reasonable threshold; to improve AlF₃ tank feeding techniques in terms of QHSE (Quality Health Safety Environment). To achieve this goal, the adopted methodology begins with the use of the DMAAC approach associated with the Lean manufacturing tools, which will limit the waste of aluminum fluoride in the primary aluminum manufacturing process. After deploying this tool, we implemented operational solutions to limit the causes of overconsumption, designed and implemented a new correction scale and improved operational best practices. This allowed us to see the specific consumption of aluminum fluoride decreased from 40 kg to less than 30 kg per ton of aluminum produced, while maintaining the rate of excess of AlF₃ between 8.5 and 9.5%.

Keywords: Aluminum Fluoride, Consumption, Electrolysis, Improvement and Tank

1. Introduction

Aluminum is a metal with many qualities, such as its malleability, low density, resistance to oxidation and simple recycling methods that make it a widely used material in many fields [1]. Since the end of the 20th century, the production of primary aluminum has exploded thanks to the improvement of the quality and the quantity of the electric current in the series [2]. During its production, the content of the fluorinated elements of the cryolite bath must be maintained at a threshold. In most aluminum production plants, the excess rate of AlF₃ is maintained between 8.5-9.5% in order to lower the melting temperature of the cryolite and improve the Faraday yield. Thus, the electrolysis series tanks are fed daily with aluminum fluoride according to a program established by the process. But in recent years, the process of consumption of fluorinated products is not controlled because of the increase in the specific consumption of aluminum fluoride beyond 40 kg per ton of aluminum produced. Added to this is the rise in its price in the market. The study recorded in this paper will improve the process of consumption of fluorinated products, first we will present this process, and then the methodological approach used, finally the results obtained after application of the methodology.

2. Materials

2.1 Process of consumption of fluorinated products

The production of one ton of aluminum by electrolysis theoretically consumes 20 kg of aluminum fluoride (Figure 1). This consumption is due to factors such as [3] the emission in the form of hydrogen fluoride (HF) because when wet alumina is introduced into the tank, there is production of HF. Also due to the reaction of AlF₃ with Na₂O present in the alumina which produces bath. By impregnation in the ramming (structure in junk which makes it possible to isolate thermally the tank), when this one begins to crack. And finally, by the mechanical losses during various operations on tanks [4].

In the situation in which we find ourselves, the overconsumption is due to the difficulty of controlling the target of AlF₃ due to the diversity of the suppliers, the variation of the high rate of Na₂O in the alumina, the losses related to the transport and logistics of the zero level to the series, high anode effects and high overvoltage, high bath height, flight during the quilting, absence / bad coverage alumina, loss during the transfer of AlF₃ to the tank, poor condition of the collection network and the malfunction of capture centers [4].

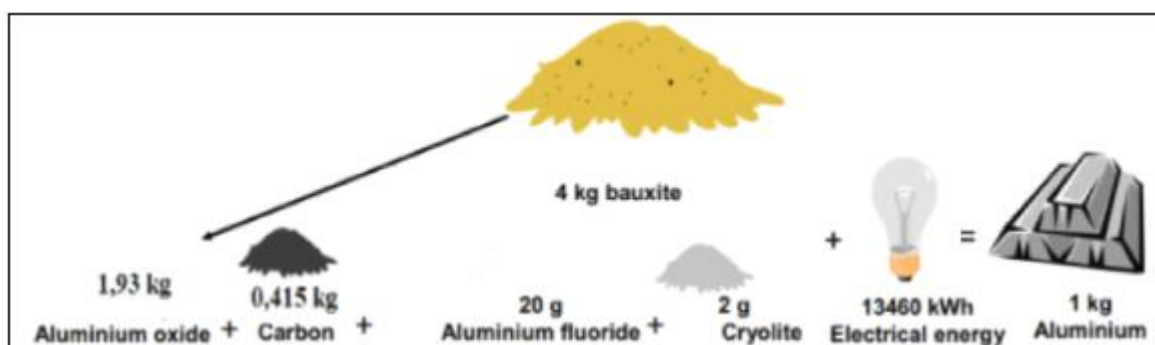


Figure 1: Production of Aluminum [5]

2.2 Process to be improved

The resolution of the problem passes through the improvement of several operations. They can be grouped in two loops [6]. The first loop goes from taking the sample to its analysis, then the results and correction in the tank. The second goes from the capture of fluorinated discharges, the fluorination to the diving of the fluorinated alumina in the tank. This is illustrated in Figure 2 [6]. Thereafter, we will use only 9 out of 274 tanks to realize our experimental design, namely: A28 - A37 - B05 - B49 - E40 - A20 - A32 - B25 - E39. The alphanumeric nomenclature of the tanks is such that the letter represents the hall of location and the number the row of the tank in the hall. They were chosen according to their geographical positions in the series.

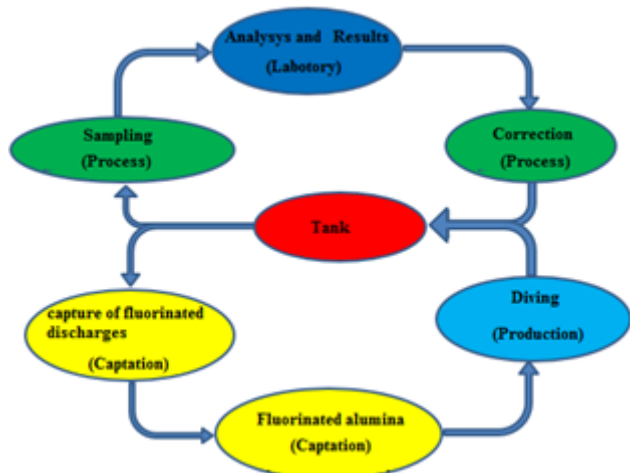


Figure 2: Process to be improved [6]

2.3 Presentation of the tool: Lean Six Sigma

To limit the waste of aluminum fluoride in the process of manufacturing primary aluminum, we used the Lean Six Sigma approach. This approach is a recent and innovative concept, which combines the increase of the speed of the processes and the increase of the quality of the products. It brings together two different but complementary approaches: Lean Manufacturing and the DMAAC approach described below [7].

Lean Manufacturing

Lean Manufacturing aims at identifying and eliminating waste through continuous improvement to achieve industrial excellence. It can be defined as a set of practices, tools and techniques designed to eliminate the causes of poor operational performance. To achieve its goal, it is necessary to act on the three main sources of inefficiency which are wastage, variability and complexity. The main tools used are VSM (visual tool for understanding critical processes and flows); the SMED (method used to decrease the time of change of productions between different products); KANBAN (production scheduling system via a simple visual system to pull the flows); the 5S (allows company workshop to be maintained clean and organized); the POKA-YOKE (simple and practical system to immediately identify that an error has been made) [7].

The DMAAC approach

It consists of a set of successive tools, which make it possible

to go from a complex problem presenting uncontrolled variables to an improvement and control of processes. It unfolds over five phases. The **Define phase**, the project manager develops the project charter, ensures the adequate support of the project. Then, general process maps are also developed by the team to facilitate the framing of the project and harmonize the perception of processes. Then the **Measure phase**, which consists of collecting data to measure the performance of the process and to quantify the problems, at the start of the project. The choice of measurement parameters is essential since they will be monitored throughout the project and will make it possible to evaluate its success. The interest of this phase is to base the decisions on real facts, that is to say encrypted. After the **Analyze phase**, it consists of giving meaning to the information collected during the measurement phase. The objective here is to determine the root cause(s) of the quality defect. We then have the **Improve phase**, which aims at identifying, evaluating and implementing the most appropriate solutions to meet the objectives developed during the "define" phase. It consists of verifying the recommendations, validating and demonstrating them, with data and graphics, a lasting improvement before the process is modified. Finally, the **Control phase**, which implies that those concerned be trained on the data collection plan and the management and interpretation methods for the key measurement graphs [7].

3. Method

3.1 Theoretical relationship between added AIF3 and excess AIF3 in the bath

The approach adopted consists of determining the variation of the level of excess AIF3 in the bath after introducing the fluoride into the tank [8]. In general, the concentration of an element in a solution is the ratio of its mass to that of the solution. In our case, the solvent is the aluminum fluoride added to the tank and the solution is the bath.

First, we will calculate the mass of the bath which is the product of the density and volume of the bath.

- The density of the bath ρ is determined using equation (1) of the Danek formula in « *Proceedings of The International Harald Oye Symposium* » [2]:

$$\rho = 2,938 - 3,373 \times 10^{-4} \times [\text{Excess AIF}_3]^2 - 4,762 \times 10^{-3} \times [\text{Al}_2\text{O}_3] - 8,466 \times 10^{-4} \times [T] \quad (1)$$

Whereas ρ is the density (kg/m^3), $[\text{Excess AIF}_3]$ is the excess rate of aluminum fluoride (%), $[\text{Al}_2\text{O}_3]$ is the Alumina concentration (%), and $[T]$ is the temperature ($^\circ\text{C}$).

- The volume of the bath is expressed by the product defined by the following equation (2):

$$V = S \times H \quad (2)$$

Whereas V is the bath volume (m^3), S is the cathode surface (m^2), H is the bath height (m).

- The bath mass is calculated using the following equation (3):

$$M = V \times \rho \quad (3)$$

Whereas M is the bath mass (kg).

Finally, we will be able to determine in equation (4), the variation of the AlF_3 excess as a function of the mass of AlF_3 brought [4].

$$\Delta\text{Ex} = \frac{\text{Mass of AlF}_3 \text{ added}}{\text{Mass of bath}} = \frac{25 \times \text{Number of bac}}{\text{Mass of bath}} \quad (4)$$

Whereas ΔEx is the AlF_3 excess rate (%).

3.2 Exploitations of chemical equations

To take stock of the chemical reactions of fluorinated products, we need to know the different inputs and outputs.

Fluorinated inputs and outputs

The principle of chemical reactions is that the mass of inputs (reagents) is equal to those of outgoing products [9]. In the case of electrolysis of aluminum alumina:

- **Fluorinated inputs** are fluorinated alumina and aluminum fluoride
- **Fluorinated outputs** are fluorinated (gas) releases and the AlF_3 portion neutralized by Na_2O to form the cryolite.

After identifying the different inputs and outputs, we can establish the balance equation.

Mass of inputs = Mass of outputs

Let's calculate the mass of AlF_3 contributed by each of the inputs and that consumed by each of the outputs for one ton of aluminum produced:

Fluorinated alumina:

It is known that 0.5% of fluorine content in alumina is equivalent to 15.9 kg of AlF_3 per ton of aluminum produced [10], but currently it is at 0.35%. We use the rule of three to have the equivalent mass of AlF_3 .

Fluorinated discharges

Fluoride discharges are only 50% captured by the capture network. Only half of the rejected will be recovered in fresh alumina. Let's calculate PRF, the AlF_3 releases contained in the exhaust gas thanks to equation (5).

$$\text{PRF} = \text{AA} \times \frac{100}{\text{Capture efficiency}} \quad (5)$$

Whereas PRF is the mass of AlF_3 contained in the exhaust gas (kg), AA is the mass of AlF_3 contained in fluorinated alumina (kg), Capture efficiency (%).

AlF_3 neutralized with Na_2O to form the bath:

The amount of neutralized AlF_3 will depend on the Na_2O content in the alumina. For a content of the order of 1000 ppm the consumption of AlF_3 will increase by 4.6 kg/t of aluminum produced [10].

Aluminum fluoride brought by the correction:

This amount of fluoride will be determined by solving the balance equation (6) as a function of the Na_2O content of the alumina.

$$\text{AA} + \text{Mass AlF}_3 = \text{PRF} + \frac{4,6 \times [\text{Na}_2\text{O}]}{1000} \quad (6)$$

Whereas Mass AlF_3 is the mass of aluminum fluoride brought by correction (kg), $[\text{Na}_2\text{O}]$ is the concentration of sodium oxide in alumina (%).

The mass of AlF_3 as a function of the Na_2O content is given by equation (7):

$$\text{Mass AlF}_3 = \text{PRF} + \frac{4,6 \times [\text{Na}_2\text{O}]}{1000} - \text{AA} \quad (7)$$

3.3 Specific consumption according to the number of bags of AlF_3

We will develop the Formula (8) which allows us to have the weekly specific consumption according to the number of bags used during the week. Let's note C_{sp} , specific consumption [9].

$$C_{sp} = \frac{\text{Mass AlF}_3}{\text{Real Production}} = \frac{\text{Number of bac} \times 25}{\text{Effic. Faraday} \times \text{Theoretical production}}$$

$$\text{Or Theoretical production} = \frac{MI}{zxFxt}$$

$$C_{sp} = \frac{\text{Number of bac} \times 25 \times z \times F \times t}{\text{Efficiency Faraday} \times M \times I} \quad (8)$$

Whereas z is the electron number exchanged = 3, F is the Faraday constant = $96484 \times 10^3 \text{ C. kmol}^{-1}$, t is the Time of electrolysis in second (s), Efficiency Faraday (%), I is the intensity (A), M is the molar mass Al (27 kg. kmol^{-1}).

3.4 Experimental Plan:

In order to confirm the theoretical results obtained, we realized an experimental plan. It took place in two phases [6]. In the first phase (first 4 weeks) it will be a question of observing the process and collecting the data. The second (last 3 weeks) will be to implement the two pilot tests. During the pilot test 1, the corrections will be made every day at the level of 1 bag per tank per day except for the weekend, which will be corrected only on Saturdays for 2 bags per tank to fill the day of Sunday. The tanks concerned will be: A28 - A37 - B05 - B49 - E40. For pilot 2, corrections will follow the usual schedule, except that no more than 2 bags per tank are corrected to ensure that no more than eight bags per week will be exceeded. The tanks concerned will be: A20 - A32 - B25 - E39.

4. Results

4.1 Theoretical relationship between added AlF_3 in the bath

Table 1 represents the intermediate results that were necessary to be calculated in order to find the relationship between the added AlF_3 and the excess AlF_3 in the bath. By using equations (1), (2), (3) and the given data of table 1, firstly, we found the density of the bath to be $2,06 \text{ g/cm}^3$. Next, the volume of the bath determined is $2,212 \text{ m}^3$ and its mass is 4566 kg by using the same table 1.

Table 1: Weighting of the selection criterion

Data					Results	
[Excess AlF_3]	[Al_2O_3]	[T]	H	S	Elements	Values
8,5 %	3 %	986°C			Density of the bath	2,06 g/cm ³
			0,1 m	22,12 m ²	Bath volume	2,212 m ³
					Bath mass	4566 kg

In theory, and using equation (4), the excess of AlF_3 should vary as indicated by the values presented in Table 2 after adding an amount of AlF_3 .

Table 2 : Variation of the AlF_3 excess rate according to the number of bags

Number of AlF_3 bag added	AlF_3 Actual Weight (kg)	AlF_3 Excess Variation (%)
1	22,5	0,5
2	45	1,0
3	67,5	1,5
4	90	2,0

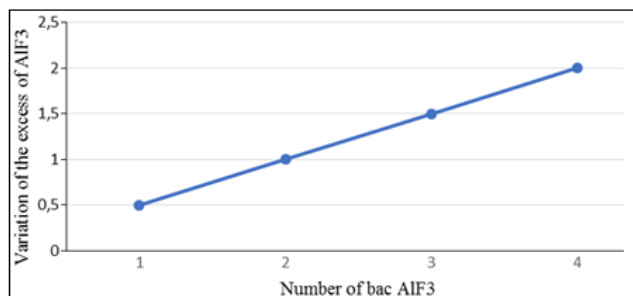
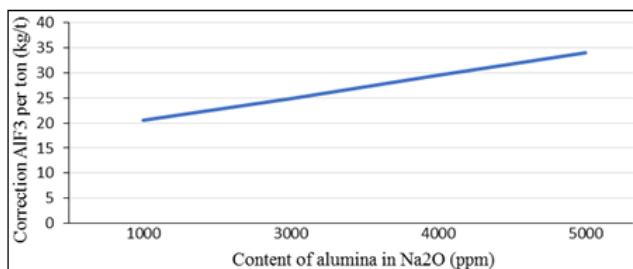
**Figure 3:** Variation of the excess of AlF_3

Figure 3 illustrates the values in Table 2 and shows that the variation of excess AlF_3 is proportional to the number of bag added but which is not always operationally true. Figure 3 also shows that, theoretically, the level of AlF_3 excess increases when the number of added bag increases.

4.2 Relationship between the correction and the Na_2O content of Alumina

Table 3: Relationship between the correction and the Na_2O content of Alumina

Na_2O content (ppm)	AlF_3 neutralized with Na_2O (kg/t)	Fixed alumina content (%)	Contribution fluorinated alumina (kg/t)	Fluorinated releases (kg/t)	Correction (kg/t)
1000	4,6	0,5	15,9	31,8	20,5
3000	13,8	0,35	11,13	22,26	24,93
4000	18,4	0,35	11,13	22,26	29,53
5000	23	0,35	11,13	22,26	34,13

**Figure 4:** Mass of AlF_3 to produce one ton of aluminum depending on the Na_2O content of the alumina

In Table 3, the bold line corresponds to the average of the Na_2O levels in the alumina encountered in the market, which requires an AlF_3 input of 29.53 kg. It is possible to have a specific consumption of less than 30 kg per ton of aluminum produced despite the current state of the series. Figure 4 illustrates Table 3 and shows that the mass of AlF_3 to produce one ton of aluminum increases with the Na_2O content of Alumina.

4.3 Specific consumption according to the number of bags of AlF_3

By using equations(5) to (8), we obtain Table 4 which shows the specific consumption of AlF_3 according to the number of bags consumed per week.

Table 4: Evolution of the specific consumption of AlF_3 according to the number of bags per week

Number of bags per tank per week	Faraday efficiency (%)	Specific consumption (kg/t Al)
4	90	13,82
5	90	17,28
6	90	20,73
7	90	24,19
8	90	27,64
9	90	31,10
10	90	34,55
11	90	38,01
12	90	41,46
13	90	44,92
14	90	48,37

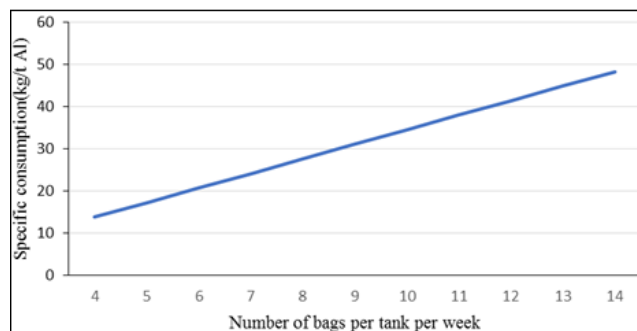
**Figure 5:** Specific consumption according to the number of bags used in a week with a Faraday yield of 90%

Table 4 further confirms that it is quite possible to have the desired specific consumption. Since according to the theoretical results, the weekly consumption would be around 7 to 8, which allows us to have a specific consumption lower than 30 kg per ton produced with a Faraday yield of 90%. This must be endorsed by an experimental plan. Figure 5 illustrates the values in Table 4 and shows that the specific consumption increases naturally with the weekly consumption of AlF_3 . And that beyond eight bags per week

the specific consumption of a tank will be higher than 30 kg per ton produced.

consumption and in Figure 7, for the evolution of the AIF3 excess rate as follows:

4.4 Results of the experimental plan

The comparative study of the first phase and the pilot tests is shown in Figure 6, for the evolution of the specific

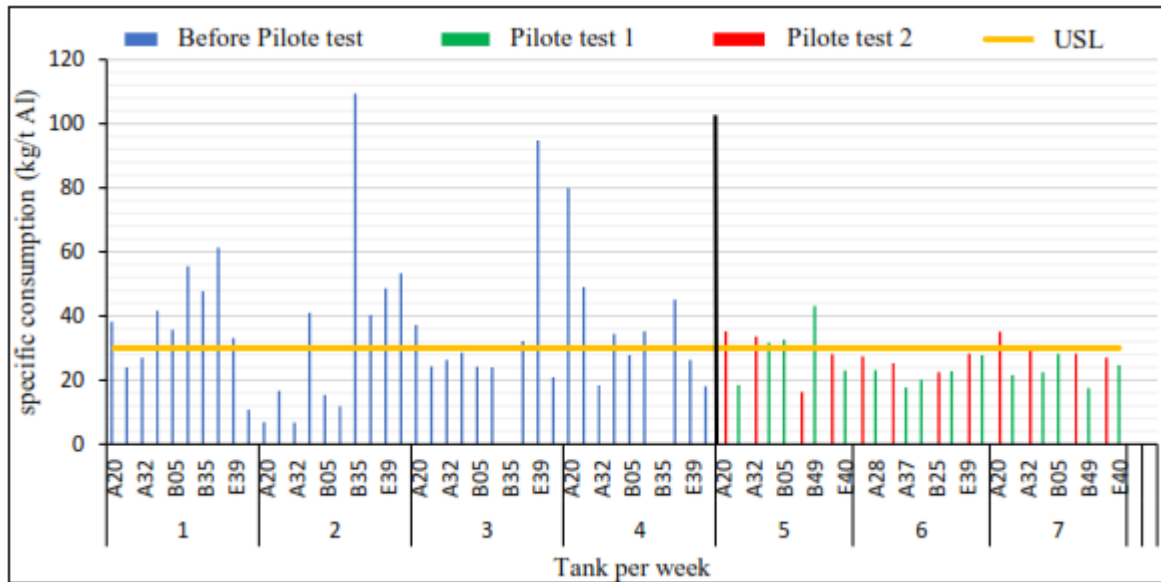


Figure 6: Specific consumption AIF3 [10]

Figure 6 is a bar graph which represents in blue the specific consumptions before the tests; in red and green those obtained during the tests. The specific consumption was reduced to less than 30 kg per ton of aluminum produced in

both tests, as most values are below the yellow line (30 kg) which represents the Upper Specification Limit (USL). Which is in perfect harmony with the theoretical results.

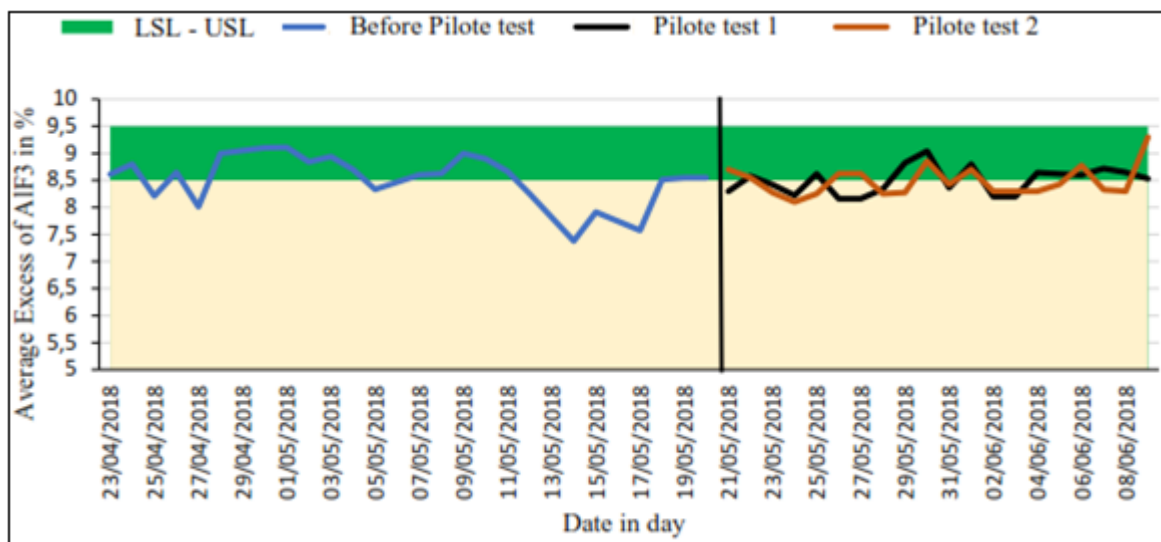


Figure 7: AIF3 excess rate [10]

Figure 7 is a diagram which shows in blue the level of excess AIF3 before the tests; in brown and black those obtained during the tests. AIF3 excess rate was maintained between the Lower Specification Limit (LSL) and the Upper Specification Limit (USL).

4.5 Operational solutions to the different causes of overconsumption

Among the operational solutions we have drawn up a quarterly training / recycling schedule for the laboratory technicians and develop management standards for the different batches of AIF3 (different suppliers). Then develop a battery / Na₂O chart in the alumina and integrate in the RCF review (Customer Support Meeting) the management

of the damages (report all anomalies with associated action plan). Update the bath casting scale taking into account alumina recycling and make it available to the SDH (Hall Supervisor) and integrate the correction into AIF3 in the SDH agenda. Update the severe criteria for evaluation of the quality of coverage and return to the head of post / SDH and evaluate the shovel solution to disembowel the bags on vats and use the squeegee to spread the AIF3. Finally equip the capture centers of autonomous compressors.

4.6 Other solutions

The three scales available do not allow us to have a specific consumption of AIF3 less than 30 kg/t of aluminum produced, which is why we have to design a new scale, which is a matrix that takes the last rates excess of AIF3, the age of the tank and the geographical position of the tank. It was designed on the basis of the results of the experimental plan and the theoretical studies. Then we proceeded to the improvement of BPO (Good Practical Practice), which will reduce fluoride losses, the quality of operations and improve the working conditions of operators. Finally, to ensure the control of the process, each operation must be constantly monitored by an operator who does not start from this operation. Reason for which it was set up a control plan on the different activities that enters the process. Added to this is a weekly monitoring dashboard.

4.7 Financial Analysis

By reducing the specific consumption of 40 to 30 kg/t of aluminum produced, savings in raw material will be achieved, which will result in financial gains. Table 5 below will determine the financial impact of the project based on this reduction.

Table 5: Financial Analysis

Comparison criteria	Current situation (40 kg/t)	Desired situation (30 kg/t)	GAP
Specific consumption (kg/t)	40	30	10
Monthly production (ton)	8000	8000	0
Estimated annual consumption of	3840	2880	960
Price per ton AIF3 (F CFA)	650 000	650 000	0
Annual cost of AIF3 (F CFA)	2 496 000 000	1 872 000 000	624 000 000

Table 5 presents the comparative analysis of the situation with a specific consumption of 30 kg/t to that of 40 kg/t. knowing the price of a ton of aluminum fluoride in the market, we determine the annual consumption of each situation knowing that in our case the annual production is estimated at 8000 tons. This is how we end up with an annual GAP of 624 million between the two situations.

5. Conclusion

The problem solved in this paper is the improvement of the method of consumption of fluorinated products in an electrolysis series. It was a question of reducing the specific consumption of AIF3 from 40 to 30 kg/t of produced aluminum, while maintaining the rate of excess of AIF3 in the bath between 8.5 and 9.5%. Firstly, it was necessary to present the problem by highlighting the major objectives to be expected from this work. Then, use the DMAAC

approach, starting with defining the process to be improved. Then through Measurement, Analysis, Improvement and Control identifying the sources of problems and ensuring the effectiveness of improvement by quantifying progress. In the application, after analyzing each of the causes of fluoride losses and theoretical studies on the reactions of fluorinated products in the bath, build an experiment plan that yielded results in the specifications of the project expectations. Subsequently, set up a new correction scale that has been implemented in the ERP of the company.

References

- [1] **VÉRONIQUE DASSYLVA-RAYMOND**, Prédiction de l'Efficacité de Courant du Procédé Hall-Héroult, *Mémoire présenté à l'université du Québec à Chicoutimi comme exigence partielle de la maîtrise en ingénierie*, Avril 2009, 143 p.
- [2] **V, DANEK, M. CHRENKOVÂ ET A. SILNY**, Proceedings of the International Harald Oye Symposium, Trondheim, Norway, 1995.
- [3] **BURKIN, A. R.**, Production of Aluminium and Alumina, *Critical Reports on Applied Chemistry*, volume 20, 1987.
- [4] **GRJOTHEIM, K., KVANDÉ, H.**, Introduction to Aluminium Electrolysis, *Aluminium-Verlag, Dtsseeldorf*, 1993, 260 p.
- [5] **PAUL CHARLES**, Aluminium-Production-Process, *Dunkerque review*, octobre 2002.
- [6] **NGUEPY TANKE PAUL VIANEY**, Amélioration du Procédé de Consommation des Produits Fluorés à la Série Electrolyse, *Mémoire présenté à l'Ecole Nationale Supérieure Polytechnique Yaoundé en vue de l'obtention du diplôme d'ingénieur de conception en génie industriel*, juillet 2018, 100 p.
- [7] **BUSINESS IMPROVEMENT**, Learn Six Sigma, méthode DMAAC, Alucam, 120 p.
- [8] **BUSINESS IMPROVEMENT**, Enseignement Aluminium Théorique, Alucam, 108 p.
- [9] **PAUL HÉROULT**, Définitions et Grands Equilibres, Electrolyse, Généralités, 150 p.
- [10] **PAUL HÉROULT**, Construction des Barèmes, Electrolyse, Construction et Démarrage, 90 p.

Author Profile

Theodore Tchotang Department of Industrial and Mechanical Engineering, National Advanced School of Engineering; University of Yaoundé I, CETIC, P.O. Box 8390, Yaoundé, Rue de Melen 3.382, Cameroon